Electrolytic treatment of azo dyes containing o,o′-dihydroxyazo complexation sites

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Abstract: The impact of structure on decolorization rate was studied for two azo dyes containing the o,o′-dihydroxyazo complexation site, Direct Red 83 and Acid Alizarin Violet N. Both dyes were investigated with and without complexed copper; the methoxylated pre-cursor of Direct Red 83 was also investigated. The dye solutions were electrolytically treated and sample conductivity, pH, and temperature were measured before and after each 60-min run. The UV–VIS absorbance spectra of samples were measured at 10 min intervals with and without quenching of chlorine residuals with sodium thiosulfate. The decolorization rate data calculated from the absorbance spectra were plotted as fraction of dye remaining, C_t/C_0, versus time, t, in seconds. First-order curves were fitted to the data, and the apparent first-order rate constant, k, was calculated for each dye. In general, the Acid Alizarin Violet N forms were decolorized more rapidly than the Direct Red 83 forms, the presence of copper protected the dyes from the continuation of indirect oxidation, and methoxylation reduced the first-order rate constant, but it did not protect the azo bond from continued indirect oxidation as was the case with copper.

Key words: azo dye, structure, electrolytic treatment, electrochemical, color, decolorization, rate constant.

Résumé : L'impact de la structure sur le taux de décoloration a été étudié pour deux colorants azoïques contenant le site de complexation o,o′-dihydroxyazo, Direct Red 83 et Acid Alizarin Violet N. Ces deux colorants ont été étudiés avec et sans cuivre complexé; le précurseur méthoxylé du Direct Red 83 a également été étudié. Les solutions de colorants ont été soumises à un traitement électrolytique et la conductivité, le pH et la température de l'échantillon ont été mesurés avant et après chaque passage de 60 min. Les spectres d'absorbance UV et visible des échantillons ont été mesurés à des intervalles de 10 min avec et sans désactivation des résidus de chlore par du thiosulfate de sodium. Les données du taux de décoloration calculées à partir des spectres d'absorbance ont été tracées sous forme de fraction de colorant restante, C_t/C_0, par rapport au temps, t, en secondes. Les courbes de premier ordre ont été ajustées aux données et la constante de vitesse apparente du premier ordre, k, a été calculée pour chaque colorant. En général, les formes Acid Alizarin Violet N ont décoloré plus rapidement que les formes Direct Red 83, la présence de cuivre a protégé les colorants de l'effet prolongé de l'oxydation indirecte et la méthoxylation a réduit la constante du taux de premier ordre, mais elle n'a pas protégé le lien azoïque de l'oxydation indirecte continue, comme ce fut le cas du cuivre.

Mots clés : colorant azoïque, structure, traitement électrolytique, électrochimique, couleur, décoloration, taux constant.

[Traduit par la Rédaction]

Introduction

Dyes are highly visible water contaminants that can be difficult compounds to treat because of their synthetic origin and often complex aromatic molecular structures. In fact, the very structures that make a compound a good dye with resistance to fading on exposure to sweat, soap, water, light, or oxidizing agents, also make the compound more stable and less amenable to biodegradation (Banat et al. 1996). Increasingly more stringent legislation in most developed countries regarding the removal of dyes from industrial effluents prior to discharge to publically-owned treatment works (POTWs) — treatment works that typically rely on biological treatment systems — is motivating research into alternative ways to treat these compounds. One such alternative is electrolytic treatment.

The use of electrolytic treatment for the decolorization of dye and textile wastewaters has been the subject of increased research interest in the last several decades, while electrolytic decomposition of recalcitrant organic compounds — especially cyanides, phenols, and thiocyanates — in industrial wastewater has been the subject of research and patents since the 1950s (Kuhn 1971). According to Abdo and Al-Ameeri (1987), the technique of anodic oxidation of wastes containing dyes was developed in the early 1970s based on research conducted in Japan. Over the last few decades, several research groups (Abdo and Al-Ameeri 1987; Lin and Peng 1993, 1996; Ogutveren and Koparal 1994; Naumczyk et al. 1996; Vlyssides et al. 1999; Jia et al. 1999; Davila-Jimenez et al. 2000; Ciardelli and Ranieri

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2001; Shen et al. 2001; Szpyrkowicz et al. 2001; Xiaong et al. 2001) have shown that electrochemical treatment of dyes is possible in a variety of reactor configurations designed to emphasize different removal mechanisms such as direct oxidation, indirect chemical oxidation, or electrocoagulation and (or) electroflocculation.
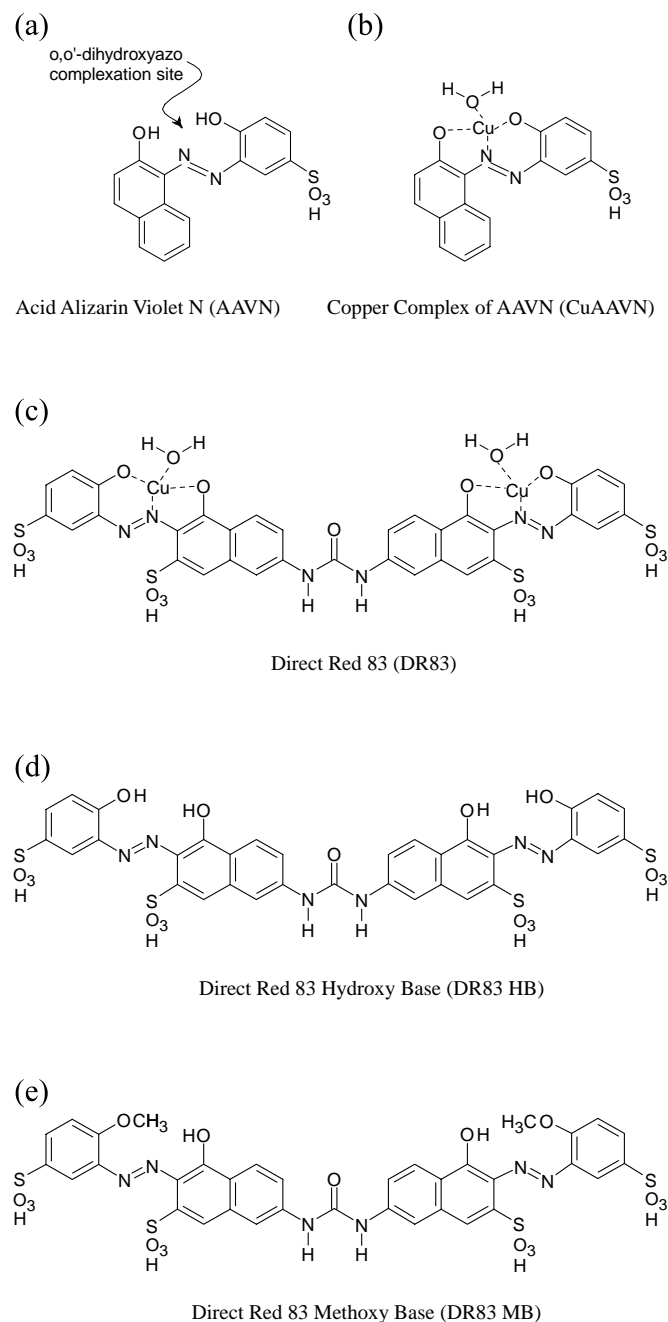
The research described in this paper expands on that knowledge base, examining the impact of chemical structure on decolorization rate for two azo dyes that contain the o,o′-dihydroxyazo complexation site, Direct Red 83 (DR83) and Acid Alizarin Violet N (AAVN). Both dyes were investigated with and without complexed copper; the methoxylated pre-cursor of Direct Red 83 was also investigated. Direct Red 83 (Cuprate (4-),[μ-[[7,7′-(carbonyldiimino)bis[4-hydroxy-3-[(2-hydroxy-5-sulfophenyl)azo]-2-naphthalenesulfonato]](8-)]]di-, tetrasodium; CAS No. 15418-16-3; Color Index No. 29225) was the primary dye of interest because it was one of five dyes provided by the US Dye Manufacturers Operating Committee (USOC) of the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) to researchers at the University of Cincinnati (UC) for evaluation as part of a technology transfer project aimed at studying the long-term fate and stability of metallized dyes in water (ETAD 1995). Acid Alizarin Violet N (4-hydroxy-3-((2-hydroxy-1-naphthalenyl)azo)-benezenesulfonic acid; also known as Solochrome Violet N and Mordant Violet 5; CAS No. 2092-55-9; Color Index No. 15670) was chosen as a second dye because it contains the same type of o,o′-dihydroxyazo complexation site as Direct Red 83, is commercially available in the uncomplexed hydroxy form, and has been used in metals complexation studies reported in the literature (Coates and Rigg 1961, 1962; Abollino et al. 1994). The structure of AAVN is similar to the structure of one of the halves of DR83 without copper, except that AAVN is formed from a 2-naphthol compound and DR83 is formed from a 1-naphthol compound. The structures of the dyes in their various forms are shown in Fig 1. Direct Red 83 contains copper in the commercially sold form, but a sample of the methoxylated precursor to the copperization step (DR83 MB) was available for comparison, and a small amount of the hydroxy form (DR83 HB) was obtained by removal of the copper with excess sulfide. Acid Alizarin Violet N is sold in the acid form, but copper was electrolytically added to the solution to form the copper-complexed form (CuAAVN), as described in the sections below.

Materials and methods

Dye source and preparation

Direct Red 83 (Fabrifast Rubine 3BLL) and Direct Red 83 methoxylated dye base (sampled from preparation of Batch #110, 1995) were obtained from the manufacturer, Fabricolor Dyes and Pigments, Paterson, New Jersey, and were purified to ~97% using a "salting out" method described by Vickerstaff (1954). Using this method, the dye (20 g/L of dye) was precipitated from hot concentrated aqueous solution by "salting it out" with sodium acetate. The precipitate was filtered, re-

Fig. 1. Structures of dyes tested.

(a)   (b)

Acid Alizarin Violet N (AAVN)   Copper Complex of AAVN (CuAAVN)

(c)

Direct Red 83 (DR83)

(d)

Direct Red 83 Hydroxy Base (DR83 HB)

(e)

Direct Red 83 Methoxy Base (DR83 MB)

dissolved, and re-precipitated several times before the purified precipitate was extracted with boiling ethyl alcohol to remove the sodium acetate. After alcohol extraction, the remaining precipitate was collected and dried to remove the ethyl alcohol and any remaining moisture, resulting in a purified sodium salt of the dye. Based on a suggestion from the technical director of the manufacturer of Direct Red 83,[2] a small amount of the copper-free hydroxy form of Direct Red 83 was obtained by adding an excess of sodium sulfide to a concentrated Direct Red 83 dye solution (20 g/L of dye), and filtering out the resulting copper

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[2] B. Bochner. 1996. Personal communication.

sulfide precipitate before a combination of glacial acetic acid (to counteract the pH rise from addition of sodium sulfide) and sodium acetate was used to salt out the dye using the Vickerstaff (1954) method. The purified dye obtained in this manner did not contain detectable amounts of copper and exhibited the spectral changes with pH consistent with those observed for purified copper-free AAVN, i.e., orange ($\lambda_{max} \sim 500$ nm) at acidic (<6) pH shifting to purple ($\lambda_{max} \sim 552$ nm) at basic(~ 8.5–12.5) pH. It should be noted that the red-colored ($\lambda_{max} \sim 519$) copper-complexed form of AAVN is stable in the pH range of 4–13.5 based on experimental observations and the predictions from MINEQL+ model (Schecher and McAvoy 1994) calculations with published AAVN ionization (Coates and Rigg 1961; Abollino et al. 1994) and Cu stability constants (Coates and Rigg 1962). The ionization and Cu stability constants for Direct Red 83 were not measured as a part of this project, but the effect of pH on color stability was experimentally observed to be negligible in the same range as AAVN (pH $\sim$ 4–12.5).
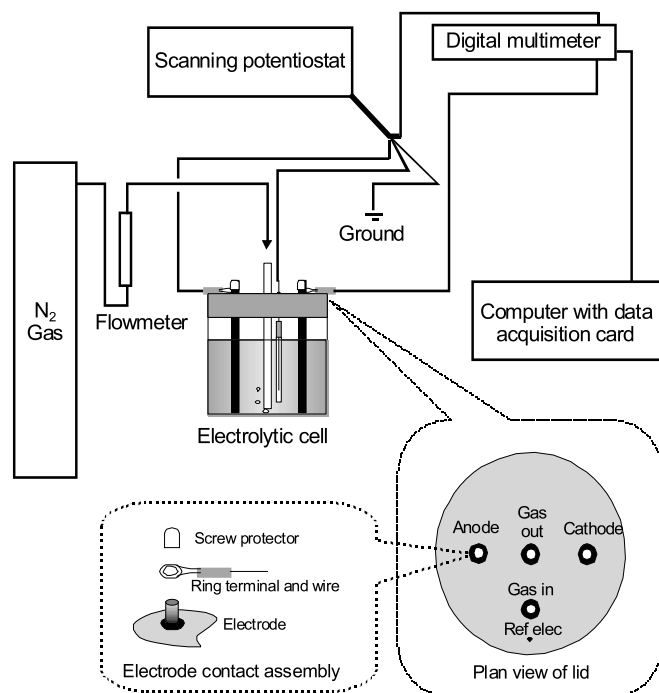
Acid Alizarin Violet N (Product No. 211001, Sigma-Aldrich, St. Louis, Missouri) was purchased in a powder form that was $\sim$50% pure, and the Vickerstaff (1954) scheme was used to purify it. The copper-complexed form of Acid Alizarin Violet N was produced in situ in the reactor (at pH 6.5) prior to the experimental run using a bare copper wire and an amount of current calculated to electrolytically convert the required amount of copper to the ionic form. (For a 300-mL volume of 20 μM AAVN, this required 23 s at 50 mA, but a slight excess was allowed by keeping the current on for 25 s.)

Experimental apparatus

The experimental apparatus consisted of an electrochemical cell in circuit with a Model 362 Scanning Potentiostat (Princeton Applied Research EG &G Instruments) and a digital multimeter (Keithley 179 TRMS Digital Multimeter equipped with a Keithley Model 1793/6423 IEEE-488 isolated output option) interfaced with a computer data acquisition system (National Instruments Corporation GPIB-PCAII NI-488.2 for DOS data acquisition board housed in a dtk FEAT 3330 personal computer with a 486 processor). An overview of the system is shown in Fig. 2.

The electrolytic cell was made from a 500-mL glass jar with a Teflon®-lined lid. The graphite anode and stainless steel cathode electrodes were 0.635 cm (0.25 in.) diameter rods cut in 9.85 cm (3.88 in.) lengths made from graphite (99% metals basis, Alpha Aesar, Stock # 10135, Lot # J12J13) and stainless steel (Type 303, Fe:Cr:Ni 73:18:9 % wt; Alpha Aesar, Stock #13473, Lot # H09J20) stock, respectively. Each rod was inserted 8.5 cm into the cell through a grommet in the lid spaced 5 cm apart center-to-center. A 25-cm length of 18-gauge hookup wire (Cat. No. 278-1226, Radio Shack, Tandy Corp., Ft. Worth, Texas) with a 0.635 cm (0.25 in.) i.d. ring terminal (#70009, Buchanan Construction Products, Inc., Hackettstown, New Jersey) soldered to it was slipped over the portion of the rod above the cell lid and held in place with a 0.635 cm (0.25 in.) rubber screw protector (Crown Bolt, Inc., Cerritos, California,

Fig. 2. Experimental apparatus.

DR#956, #30699-78068-b). The Ag–AgCl reference electrode (RE-5B, Re-order Part No. MF-2079, Bioanalytical Systems, Inc., West Lafayette, Indiana) was plugged into the socket in the lid, and a piece of glass tubing (0.63 cm (0.25 in.) i.d. $\times$ 12 cm) was inserted through the lid until the tip just missed touching the bottom of the cell. The tip of reference electrode was placed next to the gas inlet near the side of the jar, equidistant from the anode and cathode at 5 cm. The electrolytic cell was mixed using compressed nitrogen (PP grade, Wright Brothers, Inc., Cincinnati, Ohio), with the flow rate controlled at 0.1 scfm (1 scfm = 0.0004719 scms) using a two-stage regulator (Fisherbrand Model No. 10-572-D, Fisher Scientific Company) and measured with a flow meter (Precision Bore Flowrator Tube # 2-L-150/13, F. & P. Co.). Tygon-R-3603 0.635 cm (0.25 in.) i.d. tubing was used to connect the regulator, flow meter, and glass tube inserted through the lid of the cell. The working volume–anode area ratio varied slightly from 27 to 28 mL/cm^2, and the current density was held constant at 5 mA/cm^2 by adjusting the applied current when sample volume was removed.

Experimental method

The dye solutions tested were made at an equal concentration of their azo bonds in order to make the amount of color-forming groups in the dyes as close to the same as possible. Direct Red 83 and its derivative forms were tested at 10 μM and AAVN forms were tested at 20 μM. The test solution was prepared by diluting 20 mL of a concentrated stock solution of the dye (150 μM for DR83 and its derivative forms and 300 μM for AAVN) to 100 mL and adding it to the electrolytic cell jar. The electrolyte was added to the cell as 2 mL of a 1.5 N sodium

chloride (NaCl) stock plus 8 mL of a 1.5 N sodium sulfate stock (Na$_2$SO$_4$) diluted to 100 mL with purified water. The cell contents were diluted to 300 mL with purified water, making the electrolyte concentration equal to 0.01 N NaCl + 0.04 N Na$_2$SO$_4$. This salt composition was chosen to provide both direct (electrochemical) and indirect (chemical) forms of oxidation, with neither form dominating the system, based on data from related experiments on the impact of chloride concentration on the electrolytic treatment of dyes.[3]

A new graphite anode was used for each run, paired with a stainless steel cathode electrode that was thoroughly buffed with fine gauge steel wool and sand paper and cleaned with purified water (>18 MΩ) prior to the run. Nitrogen gas at 0.1 scfm was used to mix the reactor contents. Sample conductivity, pH, and temperature were measured before and after each run. The UV–VIS absorbance spectra of samples collected at 0, 10, 20, 30, 40, 50, and 60 min were measured with and without quenching of any possible chlorine residuals using sodium thiosulfate (Na$_2$S$_2$O$_3$). At each sampling time, the electrical current was briefly (<10 s) interrupted and two 5-mL samples were collected with a volumetric pipet from the mixing reactor. One sample was added to a vial containing one drop of a 2 M sodium thiosulfate solution to quench the action of any oxidizing species present in the sample; the other sample was allowed to continue reacting for at least 1 d prior to analysis. The pH of the AAVN and DR83 HB samples (pH-sensitive copper-free forms) was adjusted to $\sim$ pH 10 with 2 drops of concentrated NaOH solution just prior to analysis to shift the peaks to a consistent color. The current supplied to the system was adjusted for the loss of usable electrode surface area due to sample removal in order to maintain a constant current density of 5 mA/cm^2. The potential was noted periodically throughout the run.

Temperature and conductivity were measured using a Checkmate II meter equipped with a conductivity–TDS sensor (Cat. No. 473019, Corning Scientific Products, Corning, Inc., Corning, New York) following the manufacturer's instructions. The meter was calibrated to a potassium chloride calibration standard (12.88 mS, Cat. No. 473737, Corning Scientific Products, Corning, Inc., Corning, New York) for the conductivity measurements.

Solution pH was measured with a Fisher Scientific Accumet Research AR25 Dual Channel pH–Ion meter equipped with a Ag–AgCl combination pH electrode. The meter was calibrated prior to use each day according to manufacturer instructions using three different pH buffers, pH 4.0 (Fisher Scientific SB101-500, Lot 012970-24), pH 7.0 (Fisher Scientific SB107-500, Lot 012581-24), and pH 10.0 (Fisher Scientific SB115-500, Lot 003031-24).

The UV–VIS absorbance spectra were measured using a Hewlett-Packard Model HP8453 UV–VIS Diode Array Spectrophotometer. A 1-cm path length quartz cell was rinsed at least

once with >18 MΩ water and once with sample and then filled with fresh sample. The outside of the cell was carefully cleaned with lens paper and the cell was inserted into the cell holder of the spectrophotometer. Absorbance readings were recorded at 1 nm intervals over a range of 190–1100 nm with an integration time of 0.5 s, and the spectra were recorded two ways — as HP UV–VIS ChemStation "*.sd" files and as data imported into Microsoft Excel spreadsheet files via the electronic desktop clipboard of the data acquisition computer on the instrument.

Results

A summary of the conductivities, pH values, temperatures, and voltage ranges for each run is given in Table 1. The conductivity did not change appreciably during the course of the 1-h runs or from run to run. The final pH for one replicate of the DR83 was 9.02, an unusually high value compared to the other final pH values (pH 6.8–7.0). This value was confirmed, however, after re-checking the pH check standard. It is probable that the sample was contaminated in some way due to prior sampling for the UV–VIS absorbance spectra samples, as this phenomenon was not noted in the replicate run or the other runs performed the same day or otherwise reflected in the other data collected. The temperature fluctuated with the room temperature, dropping slightly over the course of the run, probably because of nitrogen expansion as the mixing gas bubbled through it. The potential was in the range of 2.7–2.8 V for all of these runs.

The decolorization rate data are plotted in Fig. 3, as fraction of dye remaining, C_t/C_0, versus time, t, in seconds. The concentration of dye was assumed to be proportional to the absorbance at a specified wavelength for each dye (Beers-Lambert Law) and, thus, the fraction of dye remaining was calculated as the ratio of the absorbances for the residual and initial samples at λ_{max}. Figure 4 is an example plot of the spectra with time for DR83 (with copper). Note that the spectra for the unquenched samples are marked with dashed lines. An overlay of the spectra of all five dyes at their initial concentrations with the λ_{max} used for calculations is shown in Fig. 5.

First-order curves were fitted to the data shown in Fig. 3 using the Marquardt-Levenberg algorithm in Sigma Plot 2000. The resulting apparent first-order rate constant, k, is reported in Table 2, together with the percent coefficient of variance (% CV) as a measure of error in the fit. Data for the duplicate DR83 runs were averaged and the mean was plotted with error bars that represent the two values that went into the average to give a visual sense of the run-to-run variability (less than ±10% from the mean value in all cases, and usually less than ±5%). As a practical example of the impact of dye structure on process design, the last column shown in Table 2 represents the approximate reaction times that would be required to reduce color to the point that the effluent containing that dye would meet the discharge limits for the State of Alabama (<50 American Dye Manufacturers Institute (ADMI) color units). The ADMI color unit is often used to set color discharge limits because it is

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[3] M.J. Kupferle, A. Galal, and P.L. Bishop. 2003. Electrolytic treatment of azo dye wastewaters: impact of matrix chloride content. Unpublished manuscript.

Table 1. Conductivity, pH, temperature, and potential data.

Dye studied	Conductivity (mS/cm)		pH (S.U.)		Temperature (°C)		Potential (V)
	Initial	Final	Initial	Final	Initial	Final	
DR83	4.98	5.02	6.27	9.02[*]	21.4	19.5	~2.8
DR83 dup	5.03	5.03	6.25	6.81	20.4	18.4	2.7–2.8
DR83 MB	5.03	5.00	6.51	7.00	20.7	18.2	2.7–2.8
DR83 HB	5.02	5.00	6.29	6.63	20.9	18.9	2.7–2.8
CuAAVN	4.99	5.02	6.50	6.75	20.5	18.1	2.7–2.8
AAVN	5.02	5.02	6.35	6.84	21.1	18.3	2.7–2.8

Note: DR83 dup, duplicate of DR83 run.
[*]pH check standard okay when re-checked and pH of sample was 9.03 when measured a second time, so sample vial contamination suspected.
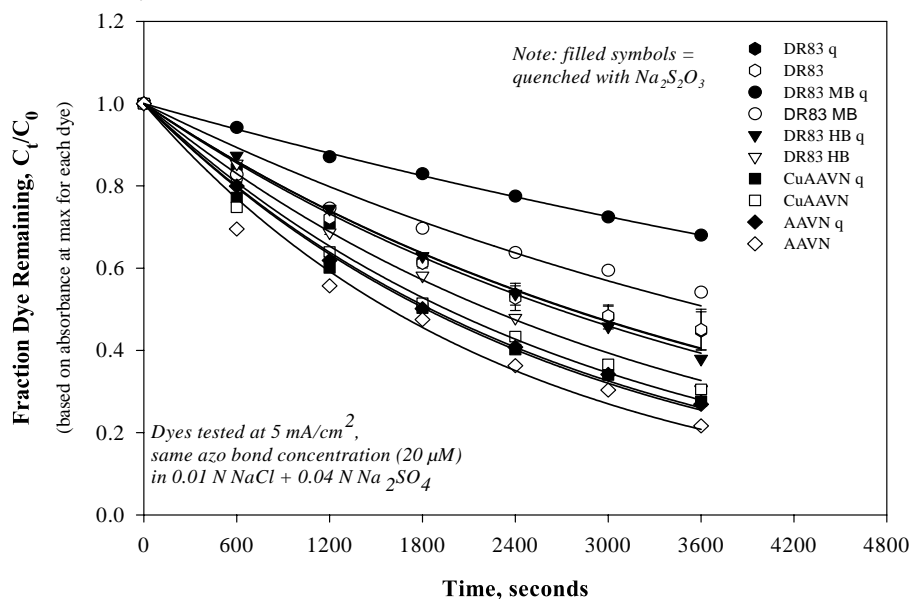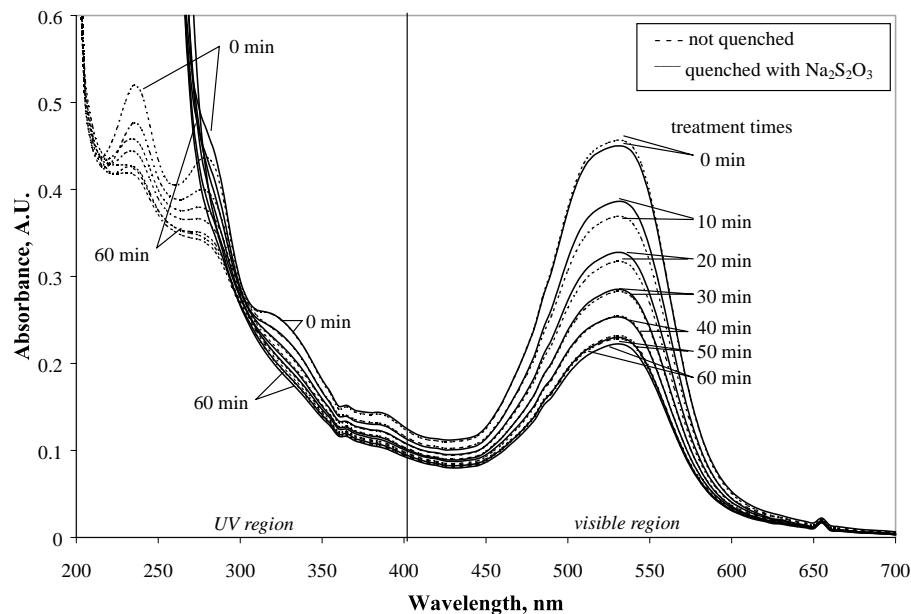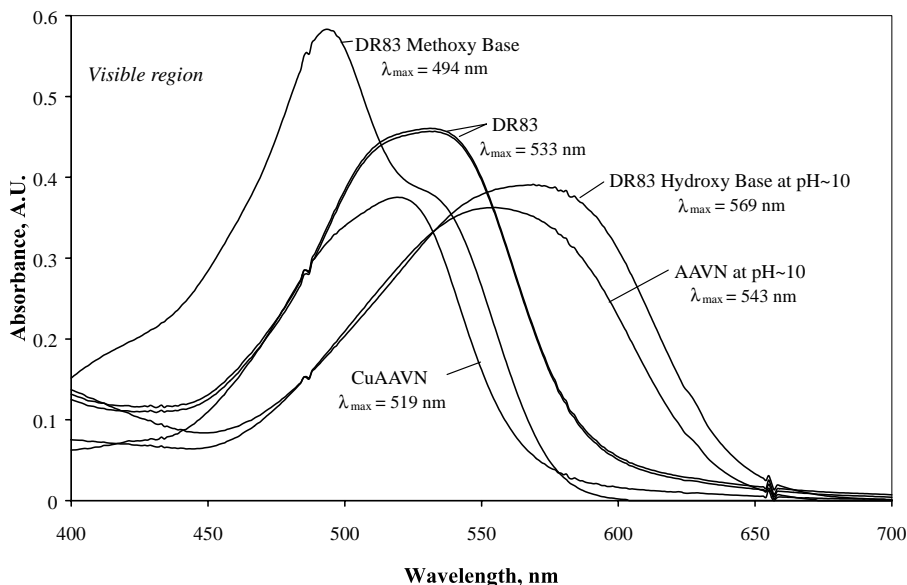
Fig. 3. Impact of dye structure on dye decolorization rate.

Fig. 4. Example UV–VIS spectra for electrolytic treatment of DR83.

Fig. 5. Comparison of initial dye spectra.

Table 2. Apparent first-order rate constants for different dyes studied.

Dye studied	Quenched using $Na_2S_2O_3$		Not quenched		
	k (s^{-1})	% CV[*]	k (s^{-1})	% CV[*]	Time (h)[†]
DR83	2.51×10^{-4}	5.56	2.52×10^{-4}	6.48	4.4
DR83 MB	1.07×10^{-4}	1.74	1.88×10^{-4}	10.1	5.9
DR83 HB	2.59×10^{-4}	2.20	3.11×10^{-4}	3.48	3.6
CuAAVN	3.80×10^{-4}	3.88	3.54×10^{-4}	5.60	3.1
AAVN	3.74×10^{-4}	2.16	4.36×10^{-4}	6.81	2.6

[*]% CV = percent coefficient of variation in parameter from curve fit.

[†]Projected batch treatment time required to meet effluent discharge limit for state of Alabama.

tied to wastewater aesthetic acceptability, representing a single-number measure of perceived sample color independent of hue. However, it is mathematically complex and is not linearly related to dye concentration, so it is not useful for dye removal calculations. The ADMI color units were estimated from spectra of measured samples using the weighted ordinates method in Method 2120 E of *Standard Methods for the Examination of Water and Wastewater* (APHA-AWWA-WEF 1995).

Discussion

In general, the first-order rate constants fell in the following ranking from largest to smallest: AAVN > CuAAVN > DR83 HB > DR83 > DR83 MB. This was true for both quenched and unquenched samples, and all rate constants were of the same order of magnitude. The rate constant for AAVN was 1.4 times larger than the rate constant for the comparable DR83 HB, for both quenched and unquenched samples. This ratio was consistent for the relationship between the copper-complexed forms as well. This difference is probably related to the more restricted stereochemistry of DR83, which has an extra -SO$_3$$^-$

group *para-* to the hydroxy group on the benzene ring portion of the dye and contains two groups the size of AAVN linked by a -NH-CO-NH- group. The position of the other hydroxy group on the naphthol portion of the two dyes (1-naphthol versus 2-naphthol) is also different, and this will affect the rate of oxidative attack on the adjacent azo bond.

The rate constants for quenched samples were very similar for each dye, with and without copper, 2.51×10^{-4} s^{-1} versus 2.59×10^{-4} s^{-1} for DR83, respectively, and 3.80×10^{-4} s^{-1} versus 3.74×10^{-4} s^{-1} for AAVN. The rate constants for the unquenched samples were a different story. They were 1.23 times larger for the uncomplexed form of the dye versus the complexed form, for both dyes. This implies that the copper-complexed form is more resistant to an indirect oxidative attack by species still present in the unquenched samples. This makes sense because the electron deficient copper atom present in the copper-complexed form attracts electrons from the oxido and azo groups, reducing the electron density at these groups which in turn retards oxidative attack at the azo position. The presence of copper in the o,o'-dihydroxyazo complexation site also prevents the tautomerization of the azo form of these dyes to the

more reactive hydrazone forms, which also retards oxidative attack (Gordon and Gregory 1987).

The results for the methoxy form of the dye were interesting. The rate constants for the non-methoxylated forms of DR83 were about 2.4 times larger than the rate constant for the methoxylated form of DR83. Methoxylation did not confer resistance to oxidative attack in the unquenched samples, however. The rate constant for the unquenched samples was 1.75 times larger than the constant for the quenched samples, but it was still lower than the rate constants for the quenched samples for the other forms of DR83 by about 0.75 times. The overall lower rate constants for the methoxylated form of DR83 are probably related to both stereochemistry and lowered reactivity of the adjacent azo bond because of the influence of the methoxy group.

Conclusion

Dye structure has an impact on decolorization rate. The first-order rate constants for Acid Alizarin Violet N were 1.4 times larger than the constants for Direct Red 83 in both the copper-free and copper-complexed forms. The absence of copper in the o,o′-dihydroxyazo complexation site of either dye increased the first-order rate constant by a factor of 1.23. The presence of copper protected the dye from the continuation of indirect oxidation at the concentration of chloride studied (0.01 N chloride and 0.04 N sodium sulfate). Methoxylation reduced the first-order rate constant to less than any of the non-methoxylated forms of dye studied, but it did not protect the azo bond from continued indirect oxidation as was the case with copper.

These results show the impact of dye structure on decolorization rate for one type of dye, azo dyes containing the o,o′-dihydroxyazo complexation site, but they highlight the fact that even relatively small changes in dye structure can affect decolorization rate. It is apparent that even just the presence of the methoxy-precursor form of Direct Red 83 from incomplete reaction or the presence of a metal-complexed AAVN formed from the presence of metal impurities will affect the overall decolorization rate of the commercial dye production waste stream. This underscores the importance of designing full-scale treatment systems with enough flexibility in operation to accommodate the batch-to-batch variability that a dye manufacturer or textile dyer will find in its effluent streams.

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